Chemical model for wire chamber aging in CF_4/iC_4H_{10} gases

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Aging of proportional counters in CF_4/iC_4H_{10} mixtures is studied as a function of gas composition. Anode surfaces are analyzed by Auger electron spectroscopy. Anode-wire deposits are formed from 95/5 and 90/10 mixtures of CF_4/iC_4H_{10}; etching of deposits occurs in 50/50 and 80/20 mixtures of CF_4/iC_4H_{10} and in pure CF_4. Gold-plated wires are resistant to aging resulting from chemical attack by CF_4, but non-gold-plated wires are too reactive for use in CF_4-containing gases. An apparent cathode aging process resulting in loss of gain rather than in a self-sustained discharge current is observed in CF_4 and CF_4-rich gases. Principles of low-pressure rf plasma chemistry are used to interpret the plasma chemistry in avalanches ($\geqslant 1$ atm, dc). To understand anode aging in CF_4/iC_4H_{10} gases, a four-part model is developed considering: (i) plasma polymerization of iC_4H_{10}; (ii) etching of wire deposits by CF_4; (iii) deposition that occurs as a result of radical scavenging in strongly etching environments; and (iv) reactivity of the wire surface. Practical guidelines suggested by the model and application of the model to other fluorine-containing gases are discussed.

I. INTRODUCTION

Wire chambers are commonly used for particle detection and tracking and find broad application in such fields as high-energy physics, astrophysics, biological diagnostics, and medical imaging.[1,2] During the course of experiments using wire chambers, however, it is common to encounter problems that limit their useful lifetime. Although wire chambers represent a mature technology, wire aging studies have been largely empirical, and the causes of wire aging are still not well understood. Wire aging studies have become more chemically oriented in recent years, however, and it has been suggested that plasma chemistry, in particular, may be a useful tool for understanding the chemical reactions that lead to wire aging.[3]

Plasma chemistry finds extensive application in microelectronics processing, which typically makes use of low-pressure (<1 Torr), rf (13.6 MHz) plasmas. While the plasma characteristics of this regime might be expected to differ from those of wire chambers (1 atm, dc), estimates of electron energies and E/p suggest that these parameters are quite similar.[4] In previous work we observed that the gaseous products formed in the avalanches in a proportional counter are, qualitatively, those expected if the chemical mechanisms in the avalanche are similar to the mechanisms in low-pressure discharges.[5] Moreover, other studies of atmospheric pressure plasmas have noted similarities to the low-pressure regime and have generally concluded that reaction mechanisms in these two pressure regimes are similar.[6–8] Despite these reasons for believing that plasma chemistry may be a useful framework with which to interpret wire aging results, no models for the aging properties of specific wire chamber gases have yet been presented. Rather, only generic plasma polymerization/plasma etching schemes have been discussed as analogs to the mechanisms responsible for wire aging phenomena. This article presents what we believe to be the first attempt to use plasma-chemical principles to identify and model the dominant chemical processes in a specific system of wire chamber gases.

There is considerable interest in the use of CF_4-based gases for wire chamber applications in future high-radiation environments such as high-energy physics experiments at the Superconducting Super Collider (SSC) and the Large Hadron Collider (LHC). This is partly because these gases typically have desirable electronic properties (e.g., high primary ionization densities,[9] high drift velocities,[9–11] and low diffusion[12]) and partly because of their expected aging properties. One gas mixture of particular interest, CF_4/iC_4H_{10} (80/20), has displayed very good aging properties[13–15] and has etched silicon-based deposits[16,17] and hydrocarbon deposits[17] from gold-plated anode wires.

It is the etching ability of CF_4/iC_4H_{10} (80/20) that is of interest here. In plasma processing, CF_4-based gases are used for both etching and deposition processes, the distinction being made by the gas with which CF_4 is mixed. In general, addition of oxygenated species shifts the chemistry of CF_4 plasmas toward etching while addition of hydrogenated species shifts the chemistry toward polymerization. Because a predominantly etching environment can be created from CF_4, it was reasonable to assume that this gas could be used to make a wire chamber gas more resistant to aging. This work confirms the etching of anode deposits on gold-plated wires with CF_4/iC_4H_{10} (80/20) and shows that etching occurs over a range of CF_4/iC_4H_{10} mixtures. However, deposition occurs for some CF_4/iC_4H_{10} mixtures. Although a complete understanding of the etching chemistry is not necessary to use CF_4/iC_4H_{10} (80/

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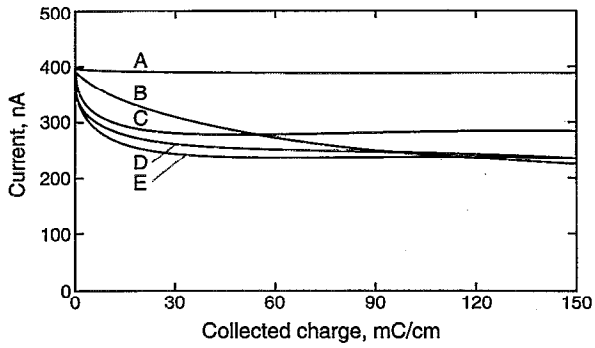

FIG. 1. Typical aging curves (current as a function of total collected charge) for CF_4 and CF_4/iC_4H_{10} gases. A: CF_4/iC_4H_{10} (80/20), Au/W wire; B: CF_4/iC_4H_{10} (80/20), Stablohm; C: CF_4, Stablohm; D: CF_4, Cu; E: CF_4, Au/W.

20),some understanding is necessary to predict the aging properties of other CF_4-based gases and to understand how their aging properties may change in the presence of trace-level impurities or intentional additives. To address this issue, we develop a chemical model to explain the observed deposition or etching in CF_4/iC_4H_{10} gases.

We have reported previously rapid aging ($\sim$50% loss of gain) when using CF_4 and smaller aging transients for CF_4/iC_4H_{10} mixtures;[18,19] Fig. 1 shows typical aging curves for CF_4 and CF_4/iC_4H_{10} (80/20) for several anode materials. In this article we present evidence that the rapid aging observed is related to chemical processes at the cathode rather than at the anode, as previously suggested.

II. EXPERIMENT

The parameters varied in this work were primarily gas composition and wire material. Gases used were CF_4 and iC_4H_{10}, encompassing the full range of mixtures from pure CF_4 to pure iC_4H_{10}. Wire materials were most often Au (plated on W), Ni, and Cu. Stablohm (an alloy consisting of 75% Ni, 20% Cr, balance Al and Cu), Al, W, and C wires were used to a lesser extent.

All gases were purchased from Matheson Gas Products (Newark, CA). Unless otherwise noted, gas mixtures were premixed by Matheson and were used as received. Pure CF_4 (semiconductor grade, minimum purity 99.999%) was filtered with a model L-60 Nanochem filter (Semi-Gas Systems, San Jose, CA). Au/W wire was purchased from Luma Metall (Kalmar, Sweden). Stablohm, Al, Cu, and Ni wires were purchased from California Fine Wire (Grover City, CA). W wire was purchased from the Rembar Company (Dobbs Ferry, NY).

A. Accelerated aging tests

To age wires in a reasonable length of time (typically 1–10 days), accelerated aging tests were performed in which the current densities on the wires were two to three orders of magnitude higher than those encountered in actual wire chamber operation. The apparatus used to collect aging data has been described elsewhere.[15,20] Briefly, proportional counters (0.95 cm i.d. copper cathode, 50-μm-diam anode wire, $\sim$10 sccm gas flow rate) were irradiated with an ^{55}Fe point source (1 mCi, 3 mm diam). The irradiated length of wire was $\sim$3.5 mm. Anode potentials varied with gas composition, but were typically 2900–3100 V. Initial wire currents were 400 ± 10 nA, corresponding to a current density of $\sim$1.1 μA/cm. The current drawn by the wire was monitored by frequent sampling. Changes in the gain can be inferred from changes in the current because the two are linearly related. Barometric pressure and gas temperature were also monitored, and corrections for changes in gain caused by variations in gas density were made according to the following formula:

$$I'_n=\frac{I_n}{(c_n)^{\alpha}}, \quad c_n=\frac{P_0T_n}{P_nT_0}, \tag{1}$$

where I is the measured current, the subscript n refers to a particular sampling, and α is the empirically determined density dependence of gas gain (typically $4<\alpha<7$). The correction factor c_n is calculated relative to the initial conditions assuming ideal-gas behavior. For the analysis of each test, the gain (current) was plotted as a function of the total charge transfer, the assumption being that the extent of aging is closely correlated with the charge transferred. Aging rates are parametrized as the normalized rate of loss of gain R,

$$R=-\frac{1}{G}\frac{dG}{dQ}=-\frac{1}{I}\frac{dI}{dQ}, \tag{2}$$

where G is gas gain, I is current, and Q is collected charge. R has units of $(\mathrm{C/cm})^{-1}$; we express R in units of %/(C/cm).

A fundamental assumption used to justify accelerated aging tests is that the aging rate is independent of the radiation dose rate. The validity of this assumption was not addressed in this work, but since the dose rates used in the accelerated tests are much higher than those occurring in a wire chamber in normal operation, caution is warranted when attempting to draw parallels between the two operating regimes. In the case of CF_4/iC_4H_{10} (80/20), however, there is evidence to suggest that aging properties are independent of dose rate.[14]

B. Pulse height

Aging was also characterized using the ^{55}Fe pulse height and energy resolution. Because the ^{55}Fe pulse height spectrum does not exhibit a narrow peak in CF_4/iC_4H_{10} gases,[21] the counter gas was alternated between CF_4-based test gases for the aging portions of the tests, and Ar/C_2H_6 (50/50) for the pulse height measurements. The ^{55}Fe spectrum in Ar/C_2H_6 has characteristic peaks that are useful for monitoring gain and gain uniformity and also displays a well-characterized degradation pattern resulting from aging.[22]

To collect pulse height (PH) data, the counter gas was changed to Ar/C_2H_6 (50/50), the 1 mCi, 3-mm-diam ^{55}Fe point source used for aging was replaced with a 500 μCi ^{55}Fe line source (collimated width $\sim$1 mm), and the anode potential was set to 2080 V. The collimated ^{55}Fe source

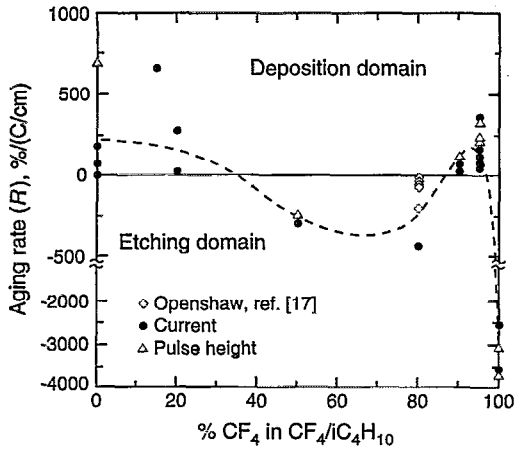

FIG. 2. Aging (recovery) rates for Au/W wires as a function of gas composition in CF_4/iC_4H_{10} mixtures. The dashed line is for eye guidance.

was oriented perpendicularly to the wire axis so that pulse height spectra could be collected at distinct positions along the wire. Each spectrum contained ~40 000 counts, corresponding to an acquisition time of 5 min and an acquisition current of ~0.35 nA.

C. Analysis of deposits

Surface analysis of wires was performed with scanning electron microscopy (SEM) for morphology determination, and Auger electron spectroscopy (AES) for elemental identification. SEM photographs shown in this work were taken with a beam voltage of 10 kV and are at 1400× magnification. Because the AES analysis depth is only ~1 nm, argon-ion-beam sputtering of the surface was used to obtain composition-depth profiles.[23]

III. DEPOSITION AND ETCHING IN CF_4/iC_4H_{10} MIXTURES

A simple model to explain the ability of CF_4/iC_4H_{10} (80/20) to etch anode deposits relates this property to the CF_4 content of the mixture. That is, because CF_4 is the parent for the reactive species responsible for etching, the resistance to aging and the ability to etch anode deposits might, naively, be expected to correlate monotonically to the CF_4 content of the gas. It was the goal of this work to develop a general chemical model to explain the aging properties of CF_4/iC_4H_{10} gas mixtures as a function of their CF_4 content. To accomplish this, we examined the aging properties of a wide range of gas mixtures and, with the realization that etching of anode deposits may occur, sought evidence for both deposition (aging) and etching (recovery).

Aging and recovery rates for Au/W wires in CF_4/iC_4H_{10} mixtures as a function of gas composition are shown in Fig. 2. Recovery results are given in detail in Table I. The data clearly show two regions of aging and two regions of etching: a region of aging between 0% and ~30% CF_4, a region of etching between ~30% and ~85% CF_4, a region of aging between ~85% and ≲100% CF_4, and a narrow region of etching in the vicinity of ~100% CF_4. (Note that these concentration boundaries are rough estimates only.) The occurrence of the aging region between ~85% and ≲100% CF_4 was unexpected, and clearly indicates problems for the use of CF_4/iC_4H_{10} mixtures in that concentration range.

Because aging transients similar to those shown in Fig. 1 occur in gases containing >90% CF_4, aging rates determined from measurements of the current in these gases were calculated for the asymptotic region of the curve. Note that the signs and relative magnitudes of the aging rates (Fig. 2 and Table I) are of more relevance than their absolute magnitudes. The magnitudes of recovery rates, in particular, should not be viewed as definitive because etching rates are expected to depend on the composition of the deposits being etched.

We now discuss the aging properties of specific CF_4/iC_4H_{10} gas mixtures.

CF_4: Although appearing to age rapidly [Figs. 1 and 3(a)], pulse height measurements on Au/W wires indicate no aging [Figs. 3(b) and 3(c)]. Indeed, there is a slight increase in the pulse height with collected charge. In addition, AES analysis of Au/W wires aged in CF_4 reveals extremely clean surfaces, with only trace amounts of C [Fig. 4(a)]. Such traces of C are normally observed on surfaces exposed to air. Depth profiles [Fig. 4(b)] reveal no deposits in excess of atmospheric carbon contamination. The appearance of these aged wires is indistinguishable from that of new wires (Fig. 5).

Recovery in CF_4 was attempted with wires aged in CF_4/iC_4H_{10} (95/5) (see below), and was observed in the current, pulse height, and energy resolution measurements. Recovery rates were rapid [typically >1000%/(C/cm)], and full gain was restored after only 0.01 C/cm of charge.

TABLE I. Summary of recovery results for Au/W wires in CF_4/iC_4H_{10} gases. The wire recovered in the CF_4/iC_4H_{10} (80/20) was originally aged in Ar/C_2H_6 (50/50) bubbled through silicone oil; the other wires were originally aged in CF_4/iC_4H_{10} (95/5).

Recovery gas mixture CF_4/iC_4H_{10}	Aged PH (%)	Recovered PH (%)	Recovery rate, PH [%/(C/cm)]	Recovery rate, I [%/(C/cm)]	Total charge (C/cm)	Current density (μA/cm)
100/0	76	103	3700	3570	0.01	0.28
100/0	74	95	3100	2535	0.01	0.27
80/20	...	...	...	410	0.36	0.50
50/50	72	96	325	265	0.17	0.34

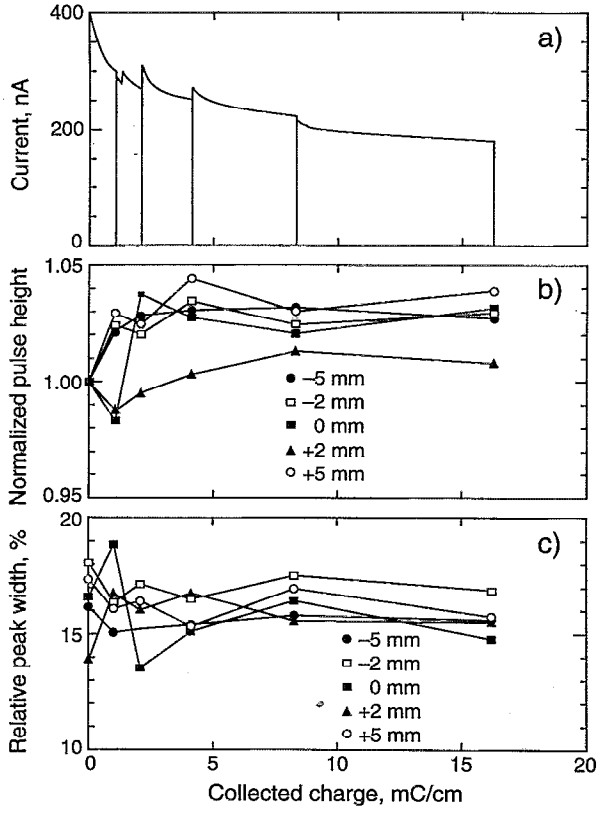

FIG. 3. Aging parameters as a function of collected charge for an Au/W wire aged in CF_4: (a) current, (b) pulse height, (c) energy resolution. Distances are relative to the center of irradiation.

The extraordinary rapidity of this recovery is an indication of the efficacy of the etching reactions in CF_4. Other workers have observed no anode aging in CF_4 (Ref. 24) or in $Xe/CF_4/CO_2$ (70/20/10).[25]

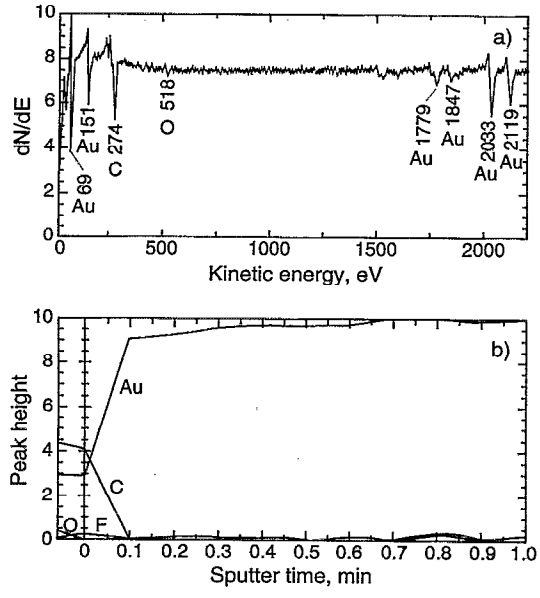

FIG. 4. (a) AES spectrum and (b) depth profile of Au/W wire aged in CF_4.

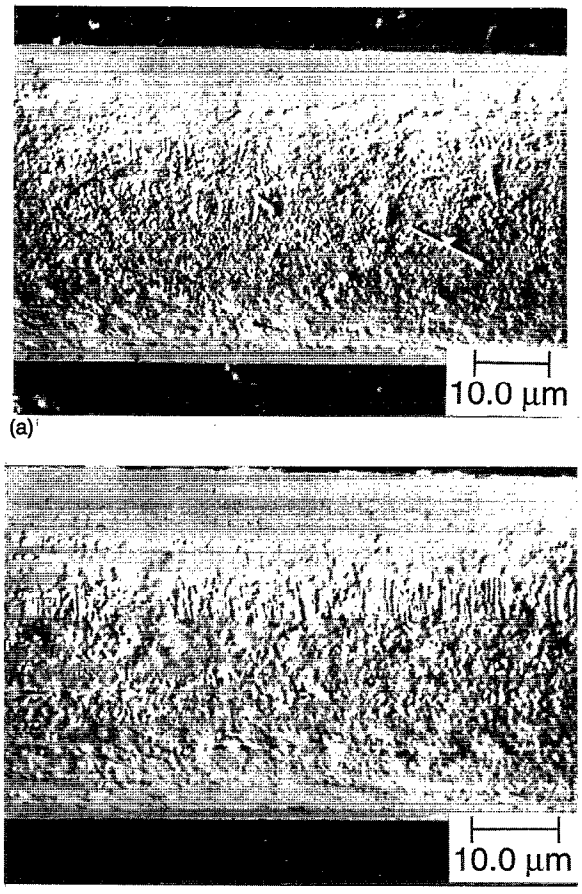

FIG. 5. Photos of Au/W wires: (a) new, (b) aged in CF_4.

Nongold wires studied (Al, Cu, Ni, Stablohm) exhibit severe degradation of the pulse height (Fig. 6) and react to form a metal fluoride on the surface when aged in CF_4. Figure 7 shows typical AES depth profiles of aged Cu and Al wires; the presence of metal fluorides is clearly indicated by the correlation between fluorine and the metal and by the absence of carbon. The morphology of the metal fluorides is smooth, resembling that of unused wires (Fig. 8). Growth of the copper fluoride is discussed further in Sec. VI. Small amounts of carbonaceous material were occasionally observed on top of the metal fluorides [e.g., Fig. 7(a)], although lack of carbon was more common [Fig. 7(b)].

CF_4/iC_4H_{10} (95/5): Heavy carbonaceous deposits are formed on Au/W wires aged in this gas mixture [Fig. 9(a)]. Some variation in thickness with azimuthal position around the wire is evident. The AES spectrum is dominated by an intense C peak (Fig. 10); the thickness of the deposit masks the underlying metal. It is notable that the deposits are carbonaceous: The absence of fluorine indicates that they are formed from the iC_4H_{10}, without incorporation of CF_x fragments. (Because AES cannot detect elements with $Z<3$, it was not possible to determine whether these deposits were hydrocarbon or purely carbonaceous.) Depth profiling revealed a uniform composition throughout the deposit.

Heavy, rough deposits are also formed on nongold

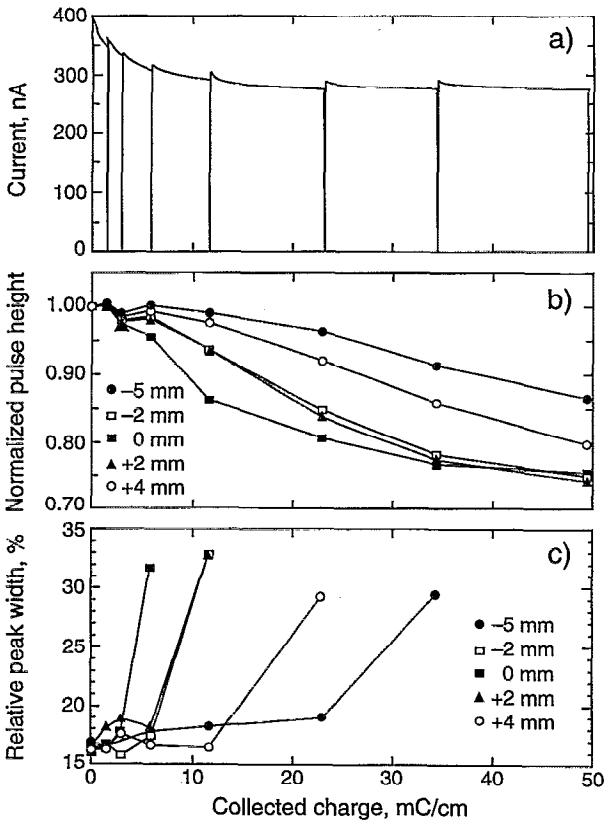

FIG. 6. Aging parameters as a function of collected charge for a Cu wire aged in CF_4: (a) current, (b) pulse height, (c) energy resolution. Distances are relative to the center of irradiation. The maximum measurable value of the energy resolution (relative peak width) is ~33%, a limit imposed by splitting of the principal ^{55}Fe peak.

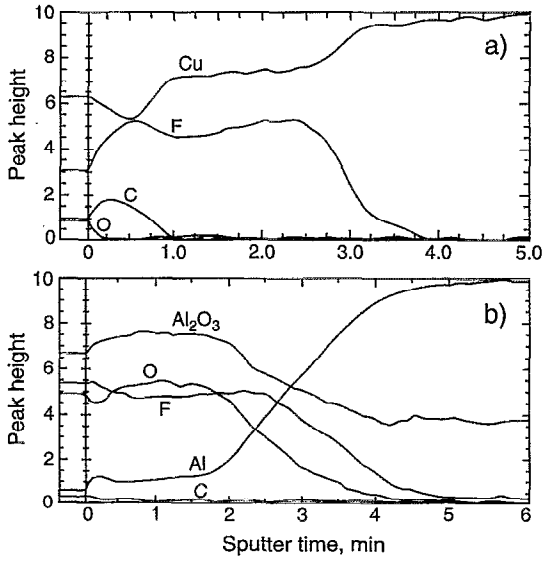

FIG. 7. AES depth profiles of (a) Cu wire and (b) Al wire aged in CF_4 showing metal fluoride films. The Al_2O_3 curve stabilizes at a nonzero value as a result of an artifact in the data acquisition process, which does not differentiate the 1378 eV peak (binding energy of Al in Al_2O_3) from the tail of the 1396 eV peak (binding energy of Al metal).

wires aged in CF_4/iC_4H_{10} (95/5); these deposits typically have distinct morphology [Fig. 11(a)]. Depth profiling revealed a stratified deposit structure, with a carbonaceous layer on top and a metal fluoride underneath (Fig. 12). The carbonaceous layer shown in this figure (~1 min of sputter time) is considerably thicker than atmospheric contamination (typically 0.1 min of sputter time), but is much thinner than the visibly heavy deposits [e.g., Figs. 9(a) and 9(b)], which have thicknesses in excess of 10 min of sputter time. Note that due to the composition dependence of the sputtering rate, there is no simple relation between the sputter time and the depth.

CF_4/iC_4H_{10} (90/10): The deposits formed on Au/W wires by the 90/10 mixture are similar, both visually and chemically, to those formed by the 95/5 mixture, although they are not as thick or as extensive. There also appears to be a sharper division in the azimuthal distribution of the deposits, with both coated and uncoated regions visible [Fig. 9(b)]. Aging of nongold wires was not investigated in this gas mixture.

CF_4/iC_4H_{10} (80/20): The appearance of Au/W wires tested in the 80/20 mixture [Fig. 9(c)] is indistinguishable from that of new wires [Fig. 5(a)]. AES analysis revealed only trace deposits (atmospheric contamination) on these wires, consistent with a previous analysis of wires whose deposits were etched in this gas mixture[17] and with the lack of aging observed in our aging tests.

Nongold wires aged in this gas mixture have heavy deposits [Fig. 11(b)]. These deposits also have a layered structure with carbonaceous material on top of a metal fluoride.

CF_4/iC_4H_{10} (50/50): Au/W wires aged in this gas mixture have only trace carbonaceous deposits, similar to those observed on wires aged in the 80/20 mixture. The aging rate measured for Au/W wires in the 50/50 mixture was $0\pm1\%/(C/cm)$ with total collected charge of 0.4 C/cm. The lack of apparent aging and of deposits suggested that this gas mixture might etch anode deposits. Indeed, recovery of a wire aged in CF_4/iC_4H_{10} (95/5) occurred at a rate of ~300%/(C/cm). Both current and pulse height recovered to within 4% of their initial values after 0.17 C/cm of collected charge. Only trace deposits were observed on a recovered wire.

Nongold wires aged in the 50/50 mixture have heavy deposits that are similar both chemically and visually to those observed on nongold wires aged in other CF_4/iC_4H_{10} mixtures.

CF_4/iC_4H_{10} (15/85) (mixed from two independently regulated flow streams): Recovery was attempted in this gas, but was largely unsuccessful. After an initial increase in the current of ~20%, the current began dropping at a rate approaching 2000%/(C/cm). This behavior is very different than that observed in the recovery tests described above, in which the current increased and then remained constant. There was an increase of 10%–15% in the pulse height, but the energy resolution was essentially unchanged from its severely degraded initial condition, suggesting that little or no recovery had occurred. The tendency of

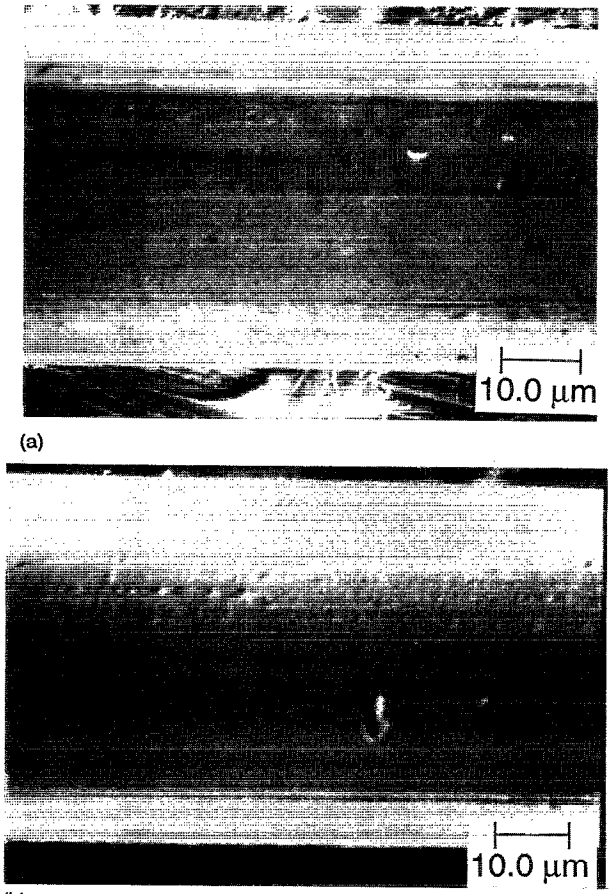

FIG. 8. Photos of Ni wires: (a) new, (b) aged in CF_4. Note the smooth surfaces. The small dark spots on the new wire are native contamination. Other nongold wires have similar appearances.

CF_4/iC_4H_{10} (15/85) to age is consistent with aging rates on the order of 100%/(C/cm) observed in CF_4/iC_4H_{10} (20/80).

iC_4H_{10}: We observed aging rates in this gas in the range 0–60% /(C/cm). Aging rates near zero indicate that little deposition occurs on the anode, consistent with previous reports of aging in iC_4H_{10}.[26] A recovery attempt with iC_4H_{10} resulted in rapid aging observed in both current and pulse height. It is possible that deposition was enhanced by the presence of deposits on the wire.

IV. CATHODE AGING EFFECTS IN CF_4

We have previously reported that rapid aging occurs in CF_4 (e.g., Fig. 1) and assumed this aging to be an anode effect.[18,19] However, this interpretation is inconsistent with the observation that CF_4 etches deposits from Au/W anode wires. Because the aging is not at the anode, we conclude that it must be on the cathode. In addition, if the observed rapid aging in CF_4 is a cathode phenomenon, the effect of the iC_4H_{10} to eliminate the aging [as in CF_4/iC_4H_{10} (80/20)] could be understood by its likely role of scavenging fluorine radicals or charge exchanging with fluorocarbon ions *en route* to the cathode.

We first verified that the transient is the result of an aging process, rather than that of a reversible process such as charge accumulation on an insulating layer, by interrupting aging tests during the transient. In all cases there was virtually no difference between the pre- and postinterruption currents, indicating that the transient is a result of some aging process in the counter. These results are summarized in Table II.

A direct means of investigating cathode aging was to separate anode and cathode effects by combining new and aged portions of counter tubes.[27] Two routes were taken. First, cathode shells of counter tubes that had been aged in CF_4 were restrung with new anode wires. Typical results

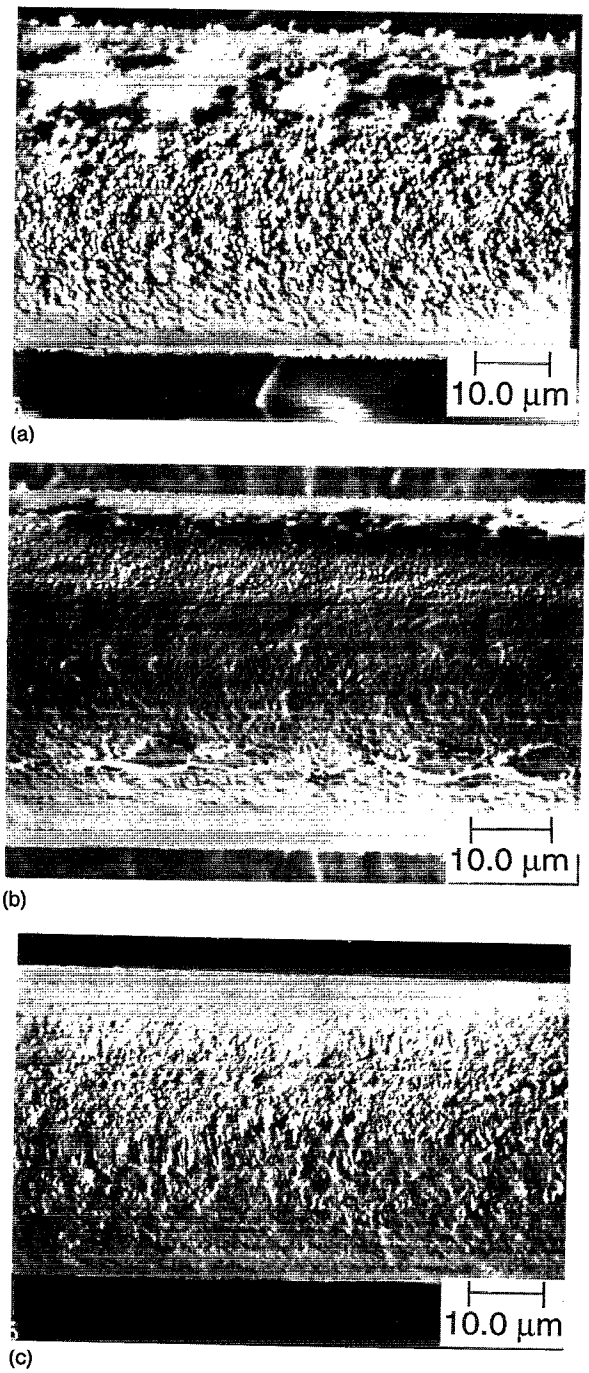

FIG. 9. Photos of Au/W wires aged in CF_4/iC_4H_{10} mixtures: (a) 95/5, (b) 90/10, (c) 80/20.

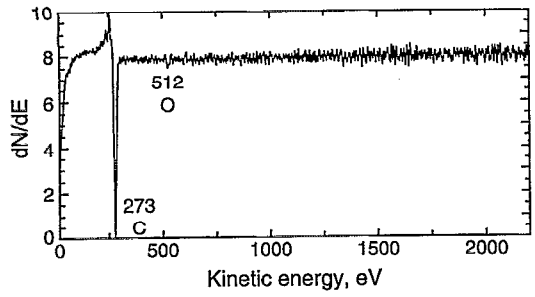

FIG. 10. AES spectrum of Au/W wire aged in CF_4/iC_4H_{10} (95/5). An intense C peak masks the underlying metal.

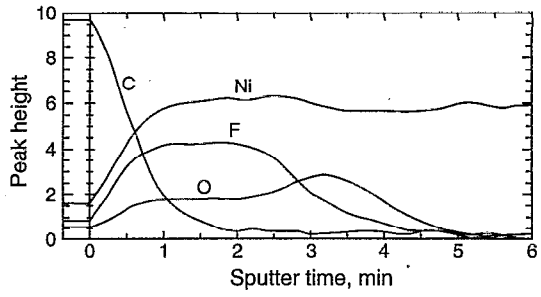

FIG. 12. AES depth profile of Ni wire aged in CF_4/iC_4H_{10} (95/5). A stratified deposit structure with a carbonaceous layer on top of a metal fluoride layer is evident.

are shown in Fig. 13(a). The expected transient is observed in the first segment of the aging, but replacement of the anode wire (point A) has essentially no effect on the current. Second, special counter tubes with replaceable cathodes were prepared and aged in CF_4. The aged cathodes were replaced while the aged anode wires were left undisturbed. As shown in Fig. 13(b) (points B and C), a large increase in the current follows replacement of the cathode. (We believe that the recovery is incomplete because only ~80% of the cathode azimuth was replaced at points B and C, with the remaining ~20% sustaining aging.) AES analysis of the aged cathode foils (removed from the counter at points B and C) revealed trace fluorocarbon deposits. These results clearly indicate that the transient is due to aging at the cathode rather than at the anode.

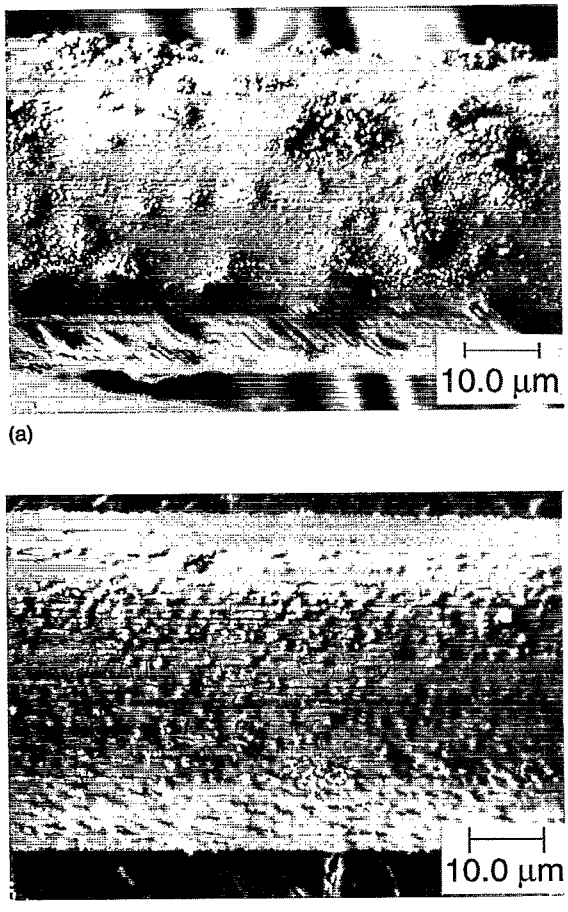

FIG. 11. Photos of nongold wires aged in CF_4/iC_4H_{10} mixtures: (a) Al wire, 95/5, (b) Ni wire, 80/20.

Further evidence that the transient reflects a cathode phenomenon comes from the observation that it is largely independent of anode material. A variety of different anode surface materials (Al, Au, C, Cu, Ni, W) including wires pretreated in an attempt to simulate aged surfaces (fluorocarbon film, copper and nickel fluorides) were aged in CF_4; a rapid transient (e.g., Fig. 1) occurred in all cases. Although the approximate independence of the aging transient to anode material could be explained if the CF_4 aging is governed solely by gas-phase kinetics (e.g., gas-phase reactions leading to fluorocarbon deposition), there is, as discussed in Sec. III, no evidence to suggest that fluorocarbon deposits form at the anode.

Possible effects of cathode material on aging in CF_4 were investigated using rectangular aluminum counter tubes with windows 1 cm in diameter. The design of these counters has been described previously.[28] Three cathode materials (Al, Au, and Ni) were used; the latter two materials were plated onto the tube and the window foil. The rapid aging transient was unchanged by the use of Au or Ni instead of Cu cathodes. In approximately half of the tests using Al cathodes, however, the magnitude of the transient was greatly reduced (Table III). Trace amounts of fluorine, probably in the form of a fluorocarbon, were observed on the Al cathode window foils from these tests; the presence of fluorocarbon deposits did not appear dependent on the magnitude of the transient (Table III). There was no indication of metal fluorides, nor was there significant spatial variation in the composition of surface deposits. SEM imaging revealed no distinct deposits; from AES depth profiling the deposit thickness was estimated at ~10 nm.

A cathode-material-dependent aging phenomenon might be understood if charge accumulation on an insulating cathode layer accounts for the decrease in current observed in CF_4. The (insulating) native aluminum oxide may be of sufficient quality that a steady-state level of charge accumulation is achieved quickly, during startup of

TABLE II. Summary of results for interruptions of aging tests with CF_4. Except where noted, CF_4 flow through the counter was maintained. The current after the interruption was corrected for gas density fluctuations [Eq. (1)] with $\alpha=6$.

Wire	Wire material	I Before (nA)	I After (nA)	ΔI (%)	Δt (h)	Comments
1	Au/W	286.4	285.9	−0.18	0.17	
1	Au/W	271.3	280.4	+3.35	0.53	open to air 0.28 h
1	Au/W	192.7	195.3	+1.35	1.22	open to air 1.05 h, forced convection
1	Au/W	193.9	195.3	+0.72	1.17	
2	Au/W	244.8	247.4	+1.06	18.02	
2	Au/W	231.6	232.4	+0.35	1.68	
2	Au/W	232.7	232.7	+0.00	3.47	
3	W	233.4	232.5	−0.39	0.20	
3	W	170.4	170.5	+0.06	0.28	apply +2080 V to shell, ground anode wire

an aging test, with the result that no transient is observed. For conducting cathode materials, charge accumulation cannot occur until a dielectric (fluorocarbon) film is formed. Because formation of such a film results from reactions in the avalanche, film growth and the consequent charge accumulation are observable over a longer time scale, after an aging test is started.

Cathode aging as a result of film formation has long been known, but is not generally considered as a phenomenon that results in loss of gain. Rather, cathode films are expected to result in field emission and a self-sustained (Malter) breakdown.[29] However, if an insulating film on the cathode were sufficiently thick that the field-emission threshold were not exceeded, the voltage drop at the cathode would reduce the effective anode potential and, hence, the gain. A voltage drop of ~ 100 V is needed to cause the $\sim 50\%$ reduction in gain typically observed for aging in CF_4. To remain below the threshold for field emission, measured to be $\sim 1.8\times 10^5$ V/cm in the counters used for these tests, a cathode film must be $\geqslant 5.6$ μm thick. An upper limit on the mass of material available for reaction can be made by relating the energy dissipated by the avalanches in the time over which the rapid aging in CF_4 occurs and the dissociation energy of the C—F bond. This corresponds to $\sim 7\times 10^{-4}$ g of material which, if distributed evenly on a cathode area of 1 cm^2, would form a layer ~ 7 μm thick. While this estimate suggests that cathode aging without self-sustained breakdowns may be a possibility, the cathode deposits observed were only ~ 10 nm, far thinner than that calculated to prevent field emission.

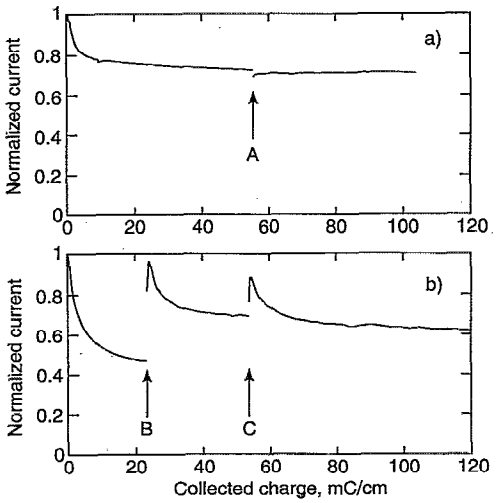

FIG. 13. Effects of new components in counters aged in CF_4: (a) new anode wire with aged cathode, (b) new cathode window with aged anode wire.

V. CHEMISTRY OF WIRE AGING

The rf glow discharges (plasmas) used in plasma processing are partially ionized gases containing ions, electrons, and neutral species in both ground and excited states. The degree of ionization is small, typically about 10^{-5} of all species, but the degree of dissociation can be quite large, sometimes exceeding 10^{-1} of all species. Because of their higher concentration, the neutrals (radicals) are the primary chemical species responsible for deposition and etching processes.

Due to the difference in mobility between ions and electrons, surfaces in contact with an rf plasma generally assume a negative potential with respect to the plasma. As a result, positive ions are accelerated into surfaces, and can have a synergistic effect on etching chemistries.[30] This process is distinctly different in an atmospheric-pressure wire chamber, where moderate energy electrons (5–10 eV) and

TABLE III. Summary of aging transients in CF_4 with Al cathodes.

Wire material	Collected charge (mC)	I_{final}/I_{max}
Cu	9.56	0.987
Cu	7.67	0.979
Cu	25.9	0.970
Cu	5.62	0.939
Cu	3.05	0.926
Au/W	33.5	0.910
Stablohm	32.2	0.887
Cu	16.8	0.761
Cu	1.59	0.620
Cu	4.59	0.570
Cu	1.76	0.520

low-energy negative ions (<1 eV) bombard the anode and near-thermal positive ions strike the cathode.

Energetic particles of a few eV can break chemical bonds at a surface, thereby creating adsorptive or reactive sites that may enhance reaction rates. Ions with energies >30 eV may cause ablation (mechanical removal of material) as a result of momentum transfer. Energetic electrons are capable of breaking chemical bonds, but due to their low mass, electron bombardment does not lead to ablation.

The chemistry in a plasma is very complex, involving a large number of reactions between many types of species and occurring both in the gas phase and at the gas/surface interface. The chemistry is further complicated by the sometimes sensitive dependence of plasmas to such variables as pressure, electrode temperature, power density, gas flow rate, gas composition, including presence of ppm- or ppb-level impurities, and reactor geometry. It was beyond the scope of this work to investigate the effects of all of these parameters. For application to wire chambers, however, knowledge of the dependence on many of these parameters is not critical because most parameters are held constant in normal operation.

A. Chemical model for aging in CF_4/iC_4H_{10} gases

One model for fluorine- and carbon-containing etch gases used in plasma processing is the F/C ratio model.[31] Rather than attempting to describe in detail the specific chemical reactions occurring in the discharge, this model views the plasma as a ratio of active fluorine species to active carbon species. That is, the F/C ratio is used as a qualitative parameter to account for the fact that etching and polymerization occur simultaneously in plasmas containing both fluorine and carbon. Anode aging in CF_4/hydrocarbon gases can be understood in terms of a four-part model based, in part, on atomic composition ratios of the gas. Because of the difficulty in accurately modeling the multitude of chemical reactions in an avalanche, the advantage of using this sort of qualitative model is obvious.

1. Polymerization

Plasma polymerization refers to the formation and deposition of polymeric material under the influence of a plasma. Plasma polymerization is believed to occur via a free-radical mechanism, which consists of three basic types of reactions: (i) initiation, in which reactive species (radicals) are formed by dissociation; (ii) propagation, in which monomers are added to a growing polymer chain; and (iii) termination, in which two radicals combine, thereby destroying the reactivity of both. Propagation reactions in plasma polymerization are believed to proceed primarily with unsaturated monomers, and there is a strong positive correlation between deposition rate and the degree of unsaturation of the monomer.[32] Deposition occurs when the polymer chain becomes sufficiently large to be involatile. There is an extensive literature on this subject,[33] and plasma polymerization has been discussed as a model for wire aging processes.[1,4,16]

With regard to small alkanes, one study of plasma polymerization has shown that polymerization rates are in the order $CH_4 > C_2H_6 > C_3H_8$,[32] from which it may reasonably be concluded that iC_4H_{10} polymerizes less readily still.

2. Etching

Etching refers to a complex set of chemical process in which gas-phase species react with a substrate to form volatile products.[34,35] Qualitatively, CF_4 dissociates to form highly reactive F and CF_x radicals at the same time that electrons are released by the avalanche. These electrons have sufficient energy (5–10 eV) to break the chemical bonds (typically 4–5 eV) in a polymeric wire deposit. Upon recombination, some fluorine may be incorporated into the polymer matrix. Under repeated avalanches, the polymer can be reduced to stable, volatile products (e.g., CF_4, CHF_3, C_2F_6), which are removed from the wire.

Fluorocarbon deposition in CF_4 plasmas is also known[36,37] but, as discussed in Sec. III, we did not observe fluorocarbon deposits at the anode. The distinction as to whether etching or deposition will occur in CF_4 depends on the plasma characteristics, although the F/C ratio model predicts CF_4, with $F/C=4$, to be strongly etching. In wire chambers, it appears that etching is the favored process.

3. Scavenging-induced deposition

Fluorine radicals in a plasma react readily with hydrogen to form HF in a process known as radical scavenging. HF is a stable molecule (5.9 eV bond energy), and it does not contribute to etching. If the scavenging reaction occurs with the hydrogen in hydrocarbon molecules rather than with free hydrogen radicals, production of HF is accompanied by production of carbon-enriched residues by reactions of the general form

$$mF + C_nH_{2n+2} \rightarrow mHF + C_nH_{2n+2-m}. \quad (3)$$

Due to their high degree of unsaturation, the carbon-enriched residues will have a high tendency to polymerize and will be comparatively involatile. The greater the carbon enrichment, the greater the probability that residues will deposit onto a wire. The degree of carbon enrichment is related to the probability that hydrogen is scavenged (i.e., is related to the CF_4/hydrocarbon or F/H ratio). Thus, extensive deposition may occur in gases with a high CF_4/hydrocarbon ratio (i.e., in gases with low hydrocarbon content).

Note that scavenging-induced deposition [reactions of the form of reaction (3)] is distinctly different than plasma polymerization. Although molecules in the avalanche are likely to undergo nearly complete fragmentation, we expect that some of the relatively long-lived fluorine radicals may migrate and react with unfragmented hydrocarbons molecules outside the avalanche region. This is especially likely when the concentration of fluorine radicals is large compared to that of other species. Thus, the molecular size of carbon-enriched residues may be correlated to the size of their parent hydrocarbons. It seems reasonable that the

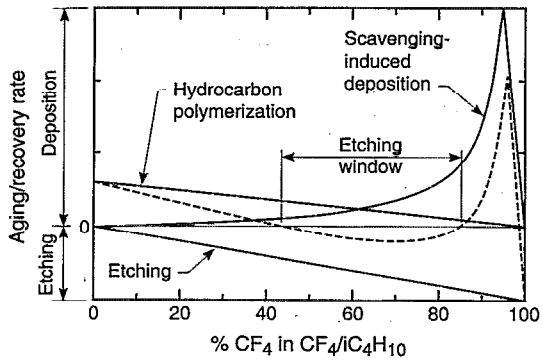

FIG. 14. Model of anode aging in CF_4/iC_4H_{10} gases showing relation between polymerization, etching, and scavenging-induced deposition.

probability that a residue will deposit onto a wire will be directly related to the size (molecular weight) of its parent. For example, a C_4 residue produced from isobutane is less volatile and thus more likely to deposit onto a wire than a C_1 residue produced from methane. (In addition to being less volatile, larger alkanes are also more carbon enriched than smaller alkanes.) Similarly, deposition is influenced by the chemical nature of the hydrocarbon (e.g., unsaturation or the presence of heteroatoms).

4. Wire surface reactivity

Many metals commonly used in wire-chamber wires react with fluorine-containing plasmas, some (Al, Cu, Ni) to form nonvolatile fluorides; others (Cr, W) to form volatile fluorides. Clear evidence of reaction of such wires with CF_4 avalanches was presented in Sec. III of this work. No evidence of such reaction was observed for Au/W wires. For practical purposes, Au is considered inert to CF_4-based plasmas, although formation of a gold fluoride in such plasmas has been reported.[38,39]

By combining the first three parts of this model, the qualitative dependence of aging on gas composition can be determined. The plasma polymerization rate of iC_4H_{10} is expected to increase with the iC_4H_{10} content of the gas, in the hypothetical case that the diluent gas, CF_4 in this case, is totally inert. Similarly, the etching rate by CF_4 is expected to increase with the CF_4 content of the gas, again hypothesizing that the diluent gas, iC_4H_{10} in this case, is totally inert. Although these two dependencies are probably nonlinear, we assume a linear dependence as shown in Fig. 14. Scavenging-induced deposition is assumed to be proportional to the CF_4/iC_4H_{10} ratio. Although this ratio becomes infinite as the iC_4H_{10} content approaches zero, it is clear that the hydrocarbon-related deposition must vanish in the limit of no hydrocarbon. Scavenging-induced deposition must therefore reach a maximum at some CF_4 concentration below 100%; it is shown in Fig. 14 as reaching a maximum at ~95% CF_4. The general trend of the data for aging behavior as a function of gas composition (Fig. 2) can be explained by the sum of these three effects, shown in Fig. 14 as the dashed line. This model explains the divisions between deposition and etching regimes, and shows that a window in which etching will occur is expected for midrange CF_4 concentrations.

Note that the relative magnitudes of the polymerization, etching, and scavenging-induced deposition effects shown in Fig. 14 are not intended to illustrate the chemistry of any particular CF_4/hydrocarbon mixture, but rather to provide a clear visual indication of the relation between the three effects. Note also that this model is only intended to explain why aging or recovery occurs in a particular gas mixture; it is not intended to predict magnitudes of aging or recovery rates. Finally, while attempting to include the dominant chemistries, this model does not include all possible chemical effects and interactions. Not included, for example, is the catalysis of plasma polymerization by halogens.[40] This effect is expected to be small, however, since conventional plasma polymerization is only slightly accelerated by CF_4.

Extensive deposition was observed on nongold wires aged in CF_4/iC_4H_{10} gas mixtures in cases when similar deposition was not observed on gold-plated wires. This difference indicates that the wire material influences the deposition mechanisms. One possible means of interaction is a loading effect, resulting from the additional reaction pathway provided by fluorination of the wire material, which reduces the effective fluorine radical concentration for all CF_4/iC_4H_{10} mixtures. With the relative strength of etching reduced, there is a greater tendency to deposit at all CF_4 concentrations. It seems unlikely, however, that a significant fraction of the gas-phase fluorine radicals would be removed by reaction with the wire. Another possibility is that there is enhanced adhesion between gas-phase carbonaceous species and metal fluorides relative to gold.

B. Other CF_4-based gases

Another gas observed to form heavy carbonaceous anode deposits was CF_4/C_2H_4 (95/5) (mixed from two independently regulated flow streams). Although pure C_2H_4 forms anode deposits, with only 5% C_2H_4 in this gas mixture, we expect scavenging-induced deposition to be the dominant deposition mechanism, by analogy to the deposition observed in CF_4/iC_4H_{10} (95/5). Indeed, the F/H ratio is larger in the CF_4/C_2H_4 mixture (F/H=19.0) than in the CF_4/iC_4H_{10} mixture (F/H=7.6), suggesting that more scavenging-induced deposition will occur in the former. However, the relative amounts of scavenging-induced deposition that may occur with C_2H_4 compared to iC_4H_{10} cannot be determined *a priori* because, although unsaturated, C_2H_4 is also a smaller molecule than iC_4H_{10}.

Previous results showing that CF_4/dimethyl ether (95/5) exhibits very little aging[41] indicate that the extent of scavenging-induced deposition is related to the chemical nature and possibly to the size of the hydrocarbon molecule. Dimethyl ether is expected to undergo relatively little scavenging-induced deposition because of its oxygen content: Oxygen can combine with carbon to form CO or CO_2, both of which are volatile.

We have previously reported rapid aging [$R \sim 120\,000\%/(C/cm)$] in $Ar/CF_4/O_2$ (50/40/10).[42]

TABLE IV. Summary of recovery results for Au/W wires in fluorine-containing gases. Deposits on these wires were formed by initial aging in CF_4/iC_4H_{10} (95/5).

Recovery gas mixture	Mixture ratio	Aged PH (%)	Recovered PH (%)	Recovery rate, PH [%/(C/cm)]	Recovery rate, I [%/(C/cm)]	Total charge (C/cm)	Current density (μA/cm)
$Ar/CF_4/O_2$	50/40/10	63	94	8400	16000	0.03	0.48
CHF_3	100	71	98	1000	990	0.09	0.43
CHF_3/CH_4	82/18	82	99	400	3830	0.05	0.43

This was an unexpected result because this gas mixture should display primarily etching characteristics and therefore be unlikely to cause deposition on anode wires. It is likely, however, that the rapid aging is a result of the same (cathode) phenomenon observed in pure CF_4. Indeed, $Ar/CF_4/O_2$ was observed to etch anode deposits created by CF_4/iC_4H_{10} (95/5) (Table IV). SEM analysis showed that a Au/W anode wire aged only in $Ar/CF_4/O_2$ was visually clean, but AES revealed that C and O (probably atmospheric contamination) and F were present on the wire surface. It should be noted that gold fluorides can be formed in CF_4/O_2 plasmas,[39] and that such fluorination, if it results from exposure to $Ar/CF_4/O_2$ avalanches, can cause anode aging in addition to any possible cathode aging that may occur.

As a diagnostic probe of the etching chemistry, it was of interest to determine whether recovery of aged wires would occur in fluorine-containing gases other than CF_4. Two such gases tested were CHF_3 and CHF_3/CH_4 (82/18). These gases were chosen without regard to their potential utility in wire chambers. Recovery beginning with a rapid decrease in the current followed by an increase in the current was observed in both of these gases (Table IV). The fact that etching occurred in these gases indicates that atomic composition rather than specific molecular configurations govern the chemistry. This is generally true for plasma etching in systems with sufficiently long residence times and serves as the basis for the F/C ratio model.

For the conditions used in the silicon etching studies of Ref. 31, etching generally occurred for $F/C > 2$. It is possible that similar general guidelines based on atomic composition ratios may be established to predict the upper limit of the etching window (Fig. 14) of prospective wire chamber gas mixtures. Table V lists several atomic composition ratios of gases investigated in this work that either deposit or etch. Using F/H as an indication of scavenging-induced deposition and F/C as an indication of etching, C/H is an indication of the deposition/etching ratio. For the gases studied, no threshold for etching is observed in the range $0.8 < F/C < 4.0$. Near the upper limit of the etching window, scavenging-induced deposition dominates for $F/H > 3$. Similarly, deposition occurs for $C/H > 1$ and etching for $C/H < 1$. Note that these guidelines are intended to apply only in the vicinity of the upper limit of the etching window. They are not intended to apply near the lower limit of the etching window, where plasma polymerization becomes more important than scavenging-induced deposition, or to the region of nearly pure CF_4, where scavenging-induced deposition cannot be assumed proportional to F/H. In addition, without more data for CF_4 in mixtures with hydrocarbons other than iC_4H_{10}, application of these guidelines to other hydrocarbons is uncertain. Finally, the C/H ratio must be used cautiously because it does not explicitly account for fluorine.

C. Other models for aging in CF_4/iC_4H_{10}

Qualitative models of wire chamber aging argue that anode deposits are formed by polymerization of radicals. In this context, it has been suggested that the good aging properties of CF_4/iC_4H_{10} (80/20) may be due to the relatively large dissociation energy of the C—F bond (5.2 eV). That is, C—F bonds may undergo less dissociation in an avalanche than other weaker bonds. With less dissociation, fewer radicals would be produced, there would be less polymerization of the radicals, less deposition, and, consequently, less aging.[4]

Another model for aging in CF_4/iC_4H_{10} gases relates to our previous interpretation of the rapid aging in CF_4 as an anode effect.[18,19] In this case, to explain why rapid aging occurred in CF_4 but not in CF_4/iC_4H_{10} (80/20), it was suggested that the iC_4H_{10} reduces formation of fluorine radicals by cooling electrons in the avalanche to temperatures below that required for dissociative electron attachment to CF_4.[19] (The peak for dissociative electron attachment to CF_4 occurs in the 7–8 eV range.[43]) With less dissociative attachment, fewer fluorine radicals would be formed, and aging effects resulting from fluorine radicals would be reduced. Although proposed to explain anode

TABLE V. Atomic composition ratios and aging properties for selected gas mixtures.

Gas mixture	Composition	Aging behavior	F/C	(F-H)/C	F/H	C/H
CF_4	100	etch	4.00	4.00	···	···
$Ar/CF_4/O_2$	50/40/10	etch	4.00	4.00	···	···
CF_4/C_2H_4	95/5	deposit	3.62	3.43	19.00	5.24
CF_4/iC_4H_{10}	95/5	deposit	3.30	2.87	7.60	2.30
CF_4/iC_4H_{10}	90/10	deposit	2.77	2.00	3.60	1.30
CHF_3	100	etch	3.00	2.00	3.00	1.00
CHF_3/CH_4	82/18	etch	2.46	0.92	1.60	0.65
CF_4/iC_4H_{10}	80/20	etch	2.00	0.75	1.60	0.80
CF_4/iC_4H_{10}	50/50	etch	0.80	−1.20	0.40	0.50
CF_4/iC_4H_{10}	20/80	deposit	0.24	−2.12	0.10	0.42

aging, this model may also be relevant to the cathode aging that we now believe occurs (Sec. IV).

However, prevention, or even reduction, of fluorine radical formation seems unlikely to be the dominant effect in CF_4/iC_4H_{10} gases. The removal of anode deposits by some CF_4/iC_4H_{10} mixtures can be explained by an etching process requiring fluorine radicals. This is especially true for removal of silicon-based deposits, which react with fluorine radicals to form volatile SiF_4. Although we have not directly observed fluorine radicals, there is ample evidence to suggest that they are the primary reactive species and play a central role in determining the properties of these gas mixtures.

D. Practical guidelines

With a model for the observed aging we are in a position to discuss some practical aspects of wire chamber operation with CF_4/iC_4H_{10} gases.

Because of possible cathode aging effects, use of pure CF_4 in a wire chamber may be detrimental. In addition, the deposition/etching balance in nearly pure CF_4 is very sensitive to gas composition, with extensive deposition possibly resulting from hydrocarbon additives or contaminants. Accordingly, it is safer to operate at a gas composition within the etching window than with nearly pure CF_4.

Nongold wires react with fluorine radicals produced in an avalanche to form metal fluorides, which may promote further deposition. Such wires are therefore unacceptable for use in CF_4-based gases. Gold wires are essentially inert to fluorine-based plasmas, and can therefore have good aging properties in CF_4-based gases. Use of gold-plated wires does not necessarily ensure good aging properties in CF_4-based gases, however, since deposition may occur on wires of any material. It should be noted that gold can be etched in plasmas of $C_2Cl_2F_4$ (Ref. 34) or $CClF_3$.[39] Accordingly, these and possibly other chlorofluorocarbon contaminants should be avoided in wire chambers.

Two issues of relevance to the choice of wire chamber gases are flammability, for the obvious safety reasons, and minimized hydrogen content, to reduce the background noise from recoil protons in neutron radiation backgrounds. These criteria both demand reduced hydrocarbon content and, due to the lower limit on hydrocarbon content imposed by the range of the etching window, may therefore conflict with the desire to formulate gases that do not age. Indeed, from the viewpoint of minimizing aging, a larger hydrocarbon concentration would be preferable. Applied to CF_4/iC_4H_{10}, the guidelines proposed in Sec. V B (that deposition occurs for $F/H>3$ or for $C/H>1$) require minimum iC_4H_{10} concentrations of 11.8% or 14.3%, respectively.

We have argued that the extent to which scavenging-induced deposition contributes to aging is directly related to the size of the hydrocarbon molecule. If so, the etching window may extend to lower hydrocarbon concentrations when CF_4 is mixed with hydrocarbons smaller than iC_4H_{10}. It may therefore be possible to make CF_4/CH_4 or CF_4/C_2H_6 mixtures that are nonflammable, have low hydrogen content, and also etch wire deposits.

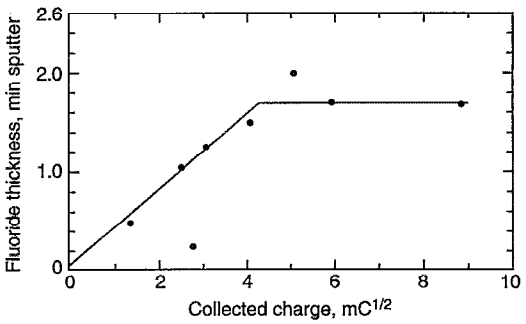

FIG. 15. Thickness of the copper fluoride film, measured by AES depth profiling, as a function of collected charge.

VI. METAL FLUORIDE FILM GROWTH ON Cu WIRES

We expect that growth of metal fluorides on nongold wires aged in CF_4 (Sec. III) may be diffusion limited. Indeed, diffusion-limited processes are well known in plasma processing occurring, for example, in etching of Si in SF_6 plasmas[44] and in growth of SiO_2 on Si in O_2 plasmas.[45] If it is assumed that growth of the metal fluoride film is purely diffusion limited, the film growth rate can be expressed as

$$\frac{dz}{dt} = -D_i k_1 \frac{dC_i}{dz}, \tag{4}$$

where D_i is the solid-state diffusivity of the fluorinating species, C_i is the near-surface gas-phase concentration of the fluorinating species, z is the thickness of the fluoride film, and k_1 is a constant that accounts for stoichiometry and fluoride density. It is permissible to use planar geometry because $z_{\max} \ll r_{\text{anode}}$. Making the assumptions that the concentration gradient is linear and that C_i is linearly related to the current,

$$\frac{dz}{dt} = -D_i k_1 \frac{C_i}{z} = -D_i k_1 k_2 \frac{I}{z}. \tag{5}$$

Using the relation $\int I\,dt = Q$, Eq. (5) becomes the classical parabolic rate equation with solution

$$z(t) = [k_3 Q + (z_0)^2]^{1/2}. \tag{6}$$

Figure 15 shows the thickness of the copper fluoride layer (measured by the time required to sputter through it) as a function of the square root of the total charge collected during exposure to the CF_4 plasma. Two distinct regions are evident: a linear region of nonzero slope, indicating diffusion-limited growth, and a region of near-zero slope, in which essentially no further growth occurs. The maximum film thickness, determined directly by SEM observation of the cross section of a bisected wire, was 450 ± 50 nm; for this film thickness, $k_3 = 1.3 \times 10^4$ nm^2/mC. Because the thickness measurements were destructive, each point shown in Fig. 15 was measured on a different wire. Errors associated with these measurements therefore include the variations in aging rates of the different wires as well as the uncertainty in the azimuthal loca-

tion of the thickest part of the deposit. For these reasons, the error in the sputter-thickness measurements is estimated to be at least $\pm 15\%$.

The reason for the limiting film thickness is not understood at present. One possibility is that the primary diffusing species are ions and that diffusion is driven by an electric field. If there is a constant potential across the film, the field strength drops as the film grows so that at some film thickness, the field strength is reduced sufficiently that further diffusion is negligible. The limiting film thickness may explain why the current drawn by nongold anodes aged in CF_4 reaches an asymptote (Fig. 1).

VII. SUMMARY AND CONCLUSIONS

We have studied the aging properties of CF_4/iC_4H_{10} gases as a function of gas mixture ratio and found two regions of deposition and two regions of etching. The existence of a region of deposition in the vicinity of $\sim 85\%$–$\lesssim 100\%$ CF_4 was unexpected, and clearly indicates problems for the use of CF_4/iC_4H_{10} mixtures in that concentration range. Specifically, this deposition regime presents a potential obstacle to the ability to formulate nonflammable gases with reduced iC_4H_{10} content.

Additional results include the following.

(a) Aging curves in CF_4 exhibit a nonlinear transient behavior in which the decrease in current is initially rapid, but then approaches a nonzero asymptote. This aging appears to occur on the cathode. It is notable that this cathode aging results in loss of gain and not in a self-sustained (Malter) discharge.

(b) Because of apparent cathode effects, the current drawn in accelerated aging tests is not a reliable indicator of anode aging for CF_4-rich gases. Accordingly, aging in such gases is best characterized by pulse height measurements and by analysis of deposits on the wire.

(c) Gold-plated wires do not age in CF_4. Other metals (Al, Cu, Ni) react with fluorine radicals in the CF_4 discharge to form metal fluorides, which appear to grow by a diffusion-limited process. For Cu wires, the effective diffusion constant $k_3 \approx 1.3 \times 10^4$ nm^2/mC, and the maximum fluoride film thickness is ~ 450 nm. Metal fluorides are observed at the interface between a carbonaceous deposit and the wire material of anodes aged in CF_4/iC_4H_{10} mixtures.

(d) A four-part chemical model of the aging processes in CF_4/iC_4H_{10} is developed to explain why some CF_4/iC_4H_{10} mixtures form anode deposits and why others etch such deposits. The model considers (i) plasma polymerization of iC_4H_{10}; (ii) etching of wire deposits by CF_4; (iii) scavenging-induced deposition, which occurs as a result of radical scavenging in strongly etching environments; and (iv) reactivity of the wire surface. We expect this model to be generally applicable to CF_4/hydrocarbon gases.

(e) Some practical implications of the model are (i) that midrange concentrations of hydrocarbons in CF_4 are generally expected to etch wire deposits, while low hydrocarbon concentrations may result in considerable aging, and (ii) that gold-plated wires are acceptable for use in CF_4-based gases while non-gold-plated wires are unacceptable.

(f) Etching is observed over a wide range of CF_4/iC_4H_{10} mixtures and in some CHF_3-based gases. The distinction as to whether etching occurs appears to be related to the atomic composition of the gas rather than to specific molecular configurations.

(g) Principles of traditional plasma chemistry (low pressure, rf) can be used to predict the plasma chemistry in wire chambers (1 atm, dc). For CF_4-based gases, the chemical mechanisms occurring in the two plasma regimes are apparently similar.

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